

age for 30 days, emulsions of lemon oil and citric acid solutions formed a number of intense off-flavor components at the expense of citral and citronellal (Schieberle and Grosch, 1988).

11.3 DISTILLED OILS

Citrus oils that are not cold-pressed and separated from emulsions by centrifugation because of their volatility may be recovered by distillation. Besides distilled lime oil (above), these oils include the volatile water and oil-phase essence from juice evaporators, d-limonene stripped during concentration of molasses, distilled oil emulsions, and the concentrated (folded) products obtained by distillation of cold-pressed oils.

11.3.1 Essence and Essence Oil

Volatile components in concentrated juice would be lost during evaporation without the vacuum stripping, condensation, rectifying, and concentration process referred to as essence recovery. Citrus fruit aroma is a complex mixture of highly volatile (acetaldehyde), moderately volatile (terpenes), and slightly volatile (sesquiterpenes) compounds. Certain constituents have intense flavor at very low concentrations (limonene thiols) or very little flavor at high concentration (ethanol). Some are soluble and desirable in the juice; others are not. Also, many of the compounds are sensitive to chemical, oxidative, thermal, or biochemical degradation, before, during, or after processing. With this scenario, the difficult objective of recovery processes is to obtain an aroma most characteristic of fresh juice.

As heated juice is flashed into the first (or other) effect of the evaporator (Chapter 5), the volatile aroma components and water are vaporized. The water becomes the steam for driving the evaporation by condensation in each successive effect. The volatile aromas in the juice vapor also pass under vacuum to the outside of the tubes of successive effects, where they are recovered. One of the early successful designs of citrus essence recovery involved trapping and condensing these entrained vapors (Brent et al., 1966). Essence recovery may also be achieved from raw fruit, juices, and vegetable products independent of juice recovery by a vapor-liquid spinning cone contacting process (ConeTech, Inc., Salinas, CA).

Most commonly, essence vapors are recovered from the first and second flash to the second and third effects of feed-forward evaporators, where concentrations are highest and temperature exposure is minimized. Inside the shell of the evaporator, volatile-containing vapors from the previous effect concentrate at some location, usually near the upper third, in the tube nests. At this point of maximum concentration, condensation and refluxing of water and the vapors may occur. It is at this point of a properly designed evaporator that volatiles are sent to the still (essence recovery unit) mounted near the top of

the evaporator. There are many evaporator designs and ways to recover the volatiles; however, most are recovered in the second or third effects of the evaporator during removal of the first 25–30% of the juice concentration process. A complete description of the juice evaporation and essence recovery process has been published for the common citrus juice TASTE evaporators (Redd et al., 1996).

When a liquid containing multicomponents is heated to its boiling point, the vapor composition is normally different from that of the liquid. The compositional difference of the two phases at equilibrium forms the basis for separation and concentration. Since many of the aromas of juice are more volatile than water, a fractional distillation process is used to rectify and concentrate them and remove water. The vapor streams [Fig. 11.3, (1)] from the noncondensable gases are collected from the second and third effects of the evaporator and sent through a valve system to the essence recovery unit. These volatiles enter the stripping column (2) of the still below the overhead condenser (3), which aids in water removal from the volatiles. This water exits through the bottom dump. The enriched volatiles and some noncondensable gases pass to a chiller (4) and into a scrubber (5). Condensed volatiles from the scrubber drain to the bottom for collection and the remaining vapor passes to a cold condenser (6) for condensate collection in a decant tank (7) at the bottom of the evaporator. The condensed decant tank product contains aqueous and oil (terpene) phases that are typically separated by decanting the oil and pumping the aqueous phase to a tank in a refrigerated room (8). Sometimes the oil-phase

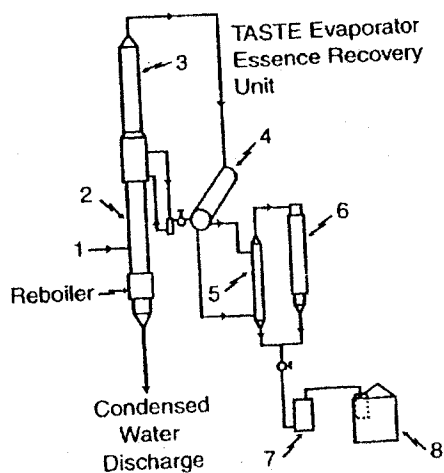


Figure 11.3 Generalized flow diagram of a TASTE evaporator citrus juice essence recovery system (Redd et al., 1996). Components include (1) vapor stream from evaporator effects, (2) stripping column, (3) overhead condenser, (4) chiller, (5) scrubber, (6) cold condenser, (7) decant tank, and (8) refrigerated tank.

essence (essence oil) is recovered by centrifuge from the cold-room product, for producing low oil, aqueous essence.

The process results in a 200- to 500-fold concentration of the volatiles, now called essence. Fold is the term used to measure the strength of the essence, for example, 1 gal of essence recovered from 200 gal of juice is defined as 200-fold. A rule-of-thumb mass balance for essence recovery yields approximately 100 lb aqueous essence (13% ethanol) and 7 lb essence oil from 1000 boxes of Valencia oranges (Johnson and Vora, 1983). The main aqueous-phase constituents of orange essence are water, >65%, ethanol, 12–25%, and methanol, 0.5–2%, depending on the condition of the juice and operation of the essence unit. The natural aqueous juice aroma constituents are present in the parts per million range, with acetaldehyde the major component. The essence oil is mostly d-limonene, 94%, valencene, >1%, myrcene, 1%, pinene, 0.5%, octanal, 0.5%, decanal, 0.6%, and so forth (Johnson and Vora, 1983). Ethanol in the essence is a major component of biochemical metabolism of the fruit and may approach 0.1–0.5% concentration in the juice from very overmature fruit. Juice methanol is a reaction product of pectinesterase activity, producing pectic acid and methanol from pectin, which also increases with fruit maturity (Chapter 5).

Essence oils and aqueous aromas have value for flavoring juices, concentrates, and beverages. Because aqueous orange essence contains >12% ethanol, but low amounts of natural aroma compounds, this product has less value than essence oil and is sometimes discarded. Acetaldehyde in the essence has value, as it helps impart fresh juice top-notes to fruit flavorings. It is possible to increase the acetaldehyde concentration by natural bioconversion from ethanol in the essence (see Chapter 14). It has been shown that acetaldehyde content of essence could be increased significantly by biomodification through use of the yeast *Pichia pastoris* (Goodrich et al., 1998). This yeast contains an enzyme complex, alcohol oxidase, that has the ability to oxidize ethanol to acetaldehyde, without requiring the expensive regenerative cofactors of alcohol dehydrogenase systems (Raymond, 1984).

Another method to concentrate aqueous essence components involves the use of reverse osmosis, with membranes capable of retaining small, highly volatile molecules such as acetaldehyde (Braddock et al., 1991). Retention of ethanol and acetaldehyde depended on the process temperature and concentration achieved but was greater than 50% at essence ethanol concentrations <10%. Larger, less volatile molecules (ethyl butyrate, hexanal, linalool, and limonene) were separated with >90% efficiency.

11.3.2 Folded Oils

11.3.2.1 Distillation and Alcohol Washing Because pure d-limonene has little or no flavor character and may readily oxidize or develop undesirable "terpeney" off-flavors, citrus oils may be concentrated to remove a portion of the limonene. These concentrated oils have improved stability and solubility in

beverages (Redd et al., 1996). The process is called folding and is measured by the ratio of the reduction in volume of the single-strength oil. For example, 5-fold oil (20 mL) will result from single-strength oil (100 mL) by removal of mostly d-limonene. Folding is commonly performed by vacuum distillation or sometimes by alcohol washing. In the example of distillation, the highest vacuum, lowest temperature, shortest time to achieve the concentration desired is necessary to avoid flavor degradation of the oil. Process conditions for manufacture of folded citrus oils by fractional distillation and alcohol washing have long been established (Bennett, 1934; Guenther, 1949). Since d-limonene is insoluble in 60–70% ethanol, orange oil may be folded by liquid–liquid extraction with alcohol. This process is achieved by slowly stirring the oil–alcohol mixture, partitioning oxygenates into the alcohol phase, and decanting the d-limonene. Use of 20 parts alcohol/1 part oil is common. Use of this process still requires distillation to remove the alcohol for reuse and recover the folded oil, if the alcohol wash, itself, is not used as a flavor.

Distillation to manufacture 5-fold, 10-fold, and 20-fold oils does not result in a linear concentration of the flavor containing aldehydes of the oil, as part may be lost during the folding. Particularly, some octanal will be lost in the terpene fraction. A 10-fold oil may be in the range of 12–15% aldehydes, having lost 20–40% of the aldehydes of the original single-strength oil. Oils concentrated more than 20-fold are usually referred to as terpeneless oils because of the low concentrations of limonene, myrcene, and pinene. Storage, handling, and use of folded oils is similar to other oils, with the exception that folded oils have higher stability used in products such as candy or baked items, which may be heated.

11.3.2.2 Adsorption Terpeneless and folded oils have been manufactured by adsorption with activated silica. Use of silica involves mixing the oil with the silica until the components are absorbed, washing the terpenes out of the silica with a nonpolar solvent, such as hexane, followed by elution of the oxygenates, pigments, and so forth with a polar solvent such as ethyl acetate (Kirchner and Miller, 1952). The solvent must be removed by distillation to recover the terpeneless oil, and the silica must either be regenerated or discarded, adding to the process cost. Flavor compounds may also be adsorbed from aqueous citrus essence by use of nonpolar polymeric materials such as styrene divinylbenzene (Bryan et al., 1977; Persson et al., 1990; Tseng et al., 1993).

11.3.2.3 Poroplast Extraction An extraction technique, which involves solute transfer between an aqueous phase passing over a nonpolar support containing the oil on a hydrophobic surface has been described (Fleisher, 1994). This process functions by washing the soluble oxygenates from the absorbed oil with aqueous alcohol in a column. When the oil is exhausted of oxygenated compounds by the alcohol, fresh oil is introduced. No difficult emulsions are

formed by this method; however, distillation of the aqueous alcohol phase is still necessary to recover the terpeneless oil.

11.3.2.4 Supercritical CO_2 Extraction Carbon dioxide, under supercritical conditions, can act as a solvent with properties dependent on the pressure and temperature, which can provide certain advantages over other separation processes. Thermally sensitive compounds can be separated at low temperatures, CO_2 is nontoxic and is easily removed from the product by releasing the pressure, and changes in pressure or temperature can change the solvent selectivity. CO_2 is also inert, nonflammable, available in high purity, and inexpensive. There have been some applications of CO_2 as an extraction solvent in the manner of alcohol washing for folding citrus oils (Japikse et al., 1987). For successful extractions, vapor pressures of oil components determine their solubility in supercritical solvents. The vapor pressure of limonene is approximately four times greater than that of linalool, an oxygenated terpene (Fig. 11.4). Since CO_2 has no dipole moment and a greater affinity for nonpolar solvents, terpenes with lower molecular weight and higher vapor pressures are more soluble in supercritical CO_2 than oxygenated flavor components (Temelli et al., 1988a,b).

Although the process is now commercial for citrus oils, extraction of the terpene fraction with CO_2 to fold the oil has its problems. The process is

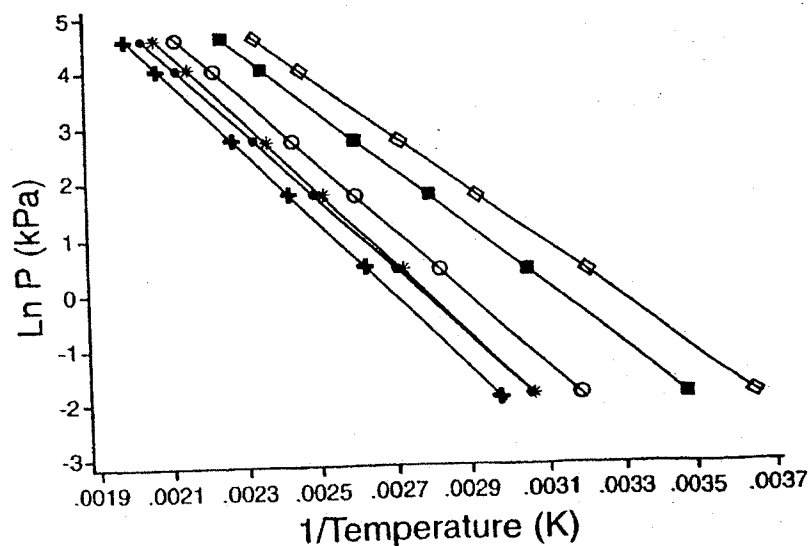


Figure 11.4 Vapor pressure vs. temperature graphs of some important components of cold-pressed orange oil: (□) d-limonene, (◆) α -pinene, myrcene, (○) linalool, (*) decanal, (●) α -terpineol, and (×) citral (plotted from data in CRC, 1986).

expensive, since vessels, columns, and equipment must withstand pressure up to 20 MPa. However, a major technical limitation is that above the critical point (31°C, 7.3 MPa), the conditions for highest selectivity of the solvent for the terpenes is near the critical temperature and not the conditions for the highest yields (Temelli et al., 1990). Because the folded oil is the product, not the extract, yield refers to terpenes extracted. There are some options, such as alcohol entrainment, which attempt to deal with this problem. One process involves use of silica to absorb oxygenates, CO₂ extraction of the terpenes, then changing pressure/temperature to extract oxygenates from the silica (Dugo et al., 1995). Folded oils produced by this method have excellent flavor and aroma qualities.

11.3.3 Encapsulated Oils

Beverage powders and certain dried foods require dried flavorings. Drying is not possible since citrus oil components are volatile liquids; thus the usual encapsulation procedure is to mix the oils with solvents, starch, gums, or corn syrup solids. This mixture may be extruded into a solvent (ethanol), then dried by evaporation (Swisher, 1962; Miller and Mutka, 1986). There are many processes and encapsulating agent combinations, with the objective of preparing good-flavored products stable to oxidative and storage changes (Anandaraman and Reineccius, 1986). Products extruded through dies are broken into small cylindrical pieces, which contain the flavor inside the matrix, protected from air and the environment of the product. The matrix itself is soluble in the product, releasing the flavor. Because the high surface area of encapsulated flavor particles may expose the oil to oxidation, an antioxidant such as BHA may be added during manufacture.

11.4 USE AND EVALUATION

The soft drink and beverage industries are the largest users of citrus oils for flavoring, followed by ice cream, cookies and desserts, confections, and chewing gum. The use level ranges from about 200 ppm in beverages to over 2000 ppm in chewing gum. World production of citrus essential oils has been estimated at greater than 50,000 mt, with 8000 mt used in soft drinks (Buchel, 1989). Production of the oil requires that the fruit be processed; thus schemes for estimating the amount of oil produced may use the values of total oil (Table 11.1) and fruit production/utilization statistics from the various growing areas (Chapter 1). It is also necessary to estimate the percent recovery from the fruit.

Evaluation of the product use level and potential flavor impact of the oils on consumers is ultimately performed by sensory evaluation at the research stage. Besides sensory techniques, analytical methods using gas chromatography/mass spectrometry (GC/MS) are useful objective techniques, which provide data related to process control as well as product stability. Books have

been written related to analytical methodology of volatile flavors in foods and beverages. The present discussion will call attention to some recent important applications of chemistry of essential oils use in foods.

For application of citrus oils to drinks and beverages, preparation of emulsions of the various oils are necessary because of the low specific gravity and insolubility of the oils in the beverage matrix. Since this matrix is mostly water and sugars and the oils are terpenes, a weighting agent (ester gum) is mixed with the oil to increase the specific gravity closer to that of the beverage. The weighting agent is usually added to the oil (1:1) to increase the specific gravity to near that of water. Gum arabic is mixed with water separately for the aqueous phase of emulsions. Since the finished oil emulsion specific gravity is still much less than that of the beverage, which contains sugar, for the emulsion to be stable, the particle size must be reduced. A recent report has given details of beverage emulsions and shown the relationship between emulsion droplet size, the weighting agent, and films of gum or modified starch, conferring long-term stability of the flavor emulsion in the product (Tan, 1998).

Computers have allowed the application of complex statistics to evaluate the volatile composition of food package headspaces. Use of multivariate statistical packages has been demonstrated to be capable of making comparisons between drinks and pure juices, shelf-life changes, and the like based on analysis of the GC chromatogram of the headspace volatiles (Shaw and Moshonas, 1997). Over 40 volatile compounds in the headspaces of fresh and processed commercial orange juices were determined and principal component analysis used to determine juice characteristics (Moshonas and Shaw, 1997). It is very difficult to determine actual volatile concentrations important to a food's flavor, and to relate this information to the human sensation of taste. Partition of volatile compounds between vapor/liquid and solid phases, followed by release during eating, has been described (Taylor, 1998).

A simple technique has been developed to concentrate the volatiles in a package headspace for GC/MS analysis. This technique, solid-phase microextraction (SPME) involves placing a fiber coated with an absorbent specific for the compounds of interest in the headspace. These compounds absorb to the fiber kinetically, depending on the vapor pressure, temperature, and time. Once absorbed, the fiber is injected into the GC/MS, where the heat desorbs the compounds onto the column for analysis (Harmon, 1997). The convenience of this procedure for preparative and analytical analysis of volatile flavors has made this the method of choice in many instances.

The GC/MS column technology has developed to the high-tech state of being capable of separation and identification of the natural enantiomers of the essential oils. The usefulness of this technology cannot be underestimated, as it has long been known that chiral discrimination of some aroma molecules depends on the enantiomeric distribution of the compound. A number of odor perceptions of enantiomers of selected flavor compounds has been published, for example, R-(-)-carvone is herbaceous and dill-like and S-(+)-carvone is characterized as spearmint (Koppenhoefer et al., 1994). The use of GC/MS

allows selecting the enantiomeric distribution of these molecules, many of which are specific in the natural product but may be altered in an adulterated flavor. Some characteristic enantiomeric ratio distributions of terpenes from citrus varieties have been published, which are useful for identifying specific oils (Mosandl et al., 1990). The reader can pursue the considerable scientific literature on this subject.

11.5 STORAGE AND HANDLING

Citrus oils should be shipped in full glass, tin-dipped, stainless steel, aluminum, or polymer-coated steel containers. Container size varies from small bottles for sample submission to 5-gal cans, 55-gal drums, or tank lots. Air should be excluded from containers by nitrogen flushing to minimize oxidation. The oil should be dry, as the presence of water will allow slow hydrolysis and formation of products such as α -terpineol. Storage at air-conditioning temperatures is adequate for most oils as wax will not precipitate under this condition. However, cold-room storage may be used for certain essences and essence oils, which do not contain the natural antioxidants of the cold-pressed oils.

Uniform color and flavor quality of oils is maintained by blending and large quantity bulking in tanks. These tanks vary in size depending on the specific oil and its demand volume but may vary from a few hundred to as much as 5000–10,000 gal. Blending of raw product at the citrus plant may help processors meet certain uniformity requirements at the point of sale. Also, bulk samples require fewer quality tests at the laboratory level. Sampling should be from well-mixed tanks or drums to represent the actual quality of the lot, ensuring the quality to the buyer.

Certain oils may be stored in specialized containers. For example, lime and lemon oil may be stored and shipped in tin-dipped drums, which adds expense to the value of these oils. Storage of some oils in polymer-coated cans and drums may be satisfactory for a short time, but many polymers (particularly polyethylene) are incompatible with the terpenes of the oil. Thus, for long-term storage, suitable containers must be used.

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